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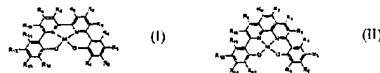
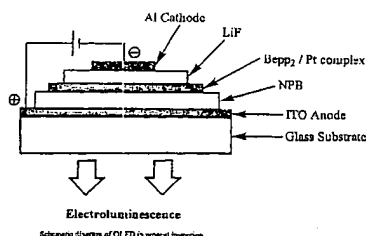
(43) International Publication Date
13 November 2003 (13.11.2003)

PCT

(10) International Publication Number
WO 03/093283 A1

- (51) International Patent Classification⁷: **C07F 15/00**
- (21) International Application Number: PCT/CN03/00221
- (22) International Filing Date: 27 March 2003 (27.03.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
10/137,272 1 May 2002 (01.05.2002) US
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
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- Published:
— with international search report
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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **ELECTROLUMINESCENT MATERIALS**



(57) Abstract: Highly luminous, thermally stable and moisture-resistant light-emitting materials derived from quadridentate ONNO-type ligands and a Group 10 metal were employed as emissive dopants in organic light-emitting devices. The dopants have molecular structures represented by the formula I and II: wherein M represents Group 10 metal (including platinum) and R_1-R_{14} are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups.

Electroluminescent Materials

Field of the Invention

5 The present invention relates to light-emitting materials, which can be deposited as a thin layer by vacuum deposition, and which can be used as effective dopants in organic light-emitting devices (OLEDs).

Background of the Invention

10 The progress of light-emitting diode (LED) over the past two decades has primarily focused on inorganic types because early development in organic light-emitting devices (OLEDs) resulted in poor fabrication and packaging, and short lifetimes. Today, gallium arsenide-based LEDs in the market are commonly available with efficiencies in some spectral
15 regions exceeding conventional filtered fluorescent lamps. However, in the development of light-emitting materials for display technology, inorganic semi-conductor materials are not compatible for large-area assembled displays.

20 Pope *et al.* at New York University demonstrated organic electroluminescence in the 1960s based on anthracene materials (*J. Chem. Phys.* 38, 2042, (1963)). Much progress have been made since the discovery of the tris(8-hydroxyquinolato)aluminum (Alq₃) based thin film device by C. W. Tang *et al.* at Kodak (*Appl. Phys. Lett.* 51, 913, (1987)). These contributed largely to the continuous discovery of new and improved electroluminescent materials. From small fluorescent molecules to conjugated polymers, many OLEDs have been shown to
25 exhibit sufficient brightness, remarkable efficiencies, good operating lifetimes and desirable ranges of color emission.

30 Organic light-emitting devices containing metal complexes are of particular interest because of their unusual chemical and electronic properties. Some compounds bearing heavy metals exhibit potential advantages for OLEDs owing to their high internal quantum efficiencies. Conventionally, fluorescent materials are employed as dopants in emissive hosts. Singlet excitons (maximum theoretical internal quantum efficiency = 25 %) are formed after recombination of hole and electron to emit electroluminescence via dipole-dipole interaction

through Förster mechanism (US Patent 6,310,360). Whereas, for heavy metal complexes, strong spin-orbit coupling can lead to singlet-triplet state mixing, which can result in high-efficiency electrophosphorescence in OLEDs (theoretical internal quantum efficiency up to 100 %) (*Nature*, 395, 151, (1998); *Synthetic Metals*, 93, 245, (1998); *Appl. Phys. Lett.* 77, 904, (2000)).

However, some phosphorescent materials have intrinsic disadvantages, such as saturation of emission sites due to excessively long lifetimes as well as triplet-triplet annihilation and concentration quenching arising from strong intermolecular interactions at high doping levels (*Phys. Rev. B.* 60, 14422, (1999)).

For example, quadridentate azomethine-zinc complexes have been used as blue light emitters in organic light-emitting devices, which exhibit maximum luminance of approximately 1000 cd/m² only (*Jpn. J. Appl. Phys.*, 32, L511 (1993); US Patent 5,432,014).

Azomethine-aluminum/gallium complexes have been employed in OLEDs as emissive materials. The current density of the device containing azomethine-gallium complex is 1 mA/cm² at 10 V and the electroluminescence is greenish blue (US Patent 6,316,130).

It is therefore desirable to develop emissive dopant materials that can permit efficient energy transfer between the host and dopant in OLEDs, while causing little or no self-quenching even at sufficiently high doping concentrations.

Summary of the Invention

Examples of objects of the present invention in embodiments thereof include:

The main objective of this invention is to prepare organic light-emitting devices (OLEDs) doped with new light-emitting materials. The devices exhibit low turn-on voltages and high luminance and efficiencies.

An object of the present invention is to provide thermally stable, moisture-resistant metal-chelated materials that can be deposited as a thin layer of known thickness by a vapor

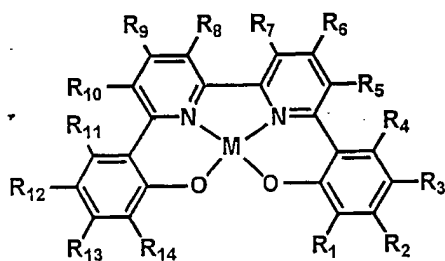
deposition process.

Further, the present invention concerns the design of high luminous dopants, which can be used at low concentration levels in light-emitting devices.

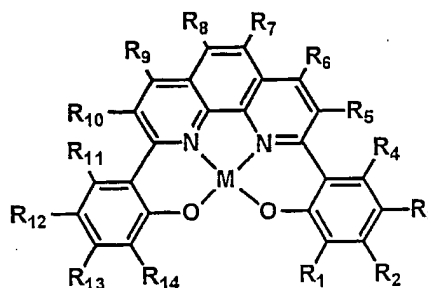
New light-emitting materials derived from quadridentate ONNO-type ligands, and a Group 10 metal (including platinum) were prepared as illustrated by formula I and II:

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I

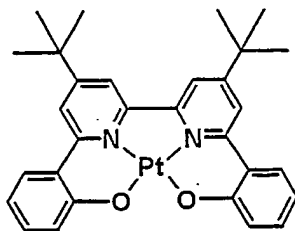


II

wherein M represents Group 10 metal (including platinum) and R_1 - R_{14} are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups.

Embodiments of the present invention includes, but is not limited to, OLEDs comprising heterostructures for producing electroluminescence which contain anode (ITO glass substance), hole transport layer (NPB (α -naphthylphenylbiphenyl amine)), matrix emissive layer [host material (beryllium bis(2-(2'-hydroxyphenyl)pyridine) (Bepp₂)) with different concentration of dopants as illustrated by formula I and II herein], charge transport layer (lithium fluoride) and cathode (aluminum metal).

The preferred embodiment as an effective dopant in the OLEDs herein is:



The present invention provides new materials for applications as emissive dopants in electroluminescent devices. The invention includes the synthetic methods for these novel complexes plus their use as light-emitting materials. The devices of the present invention can be applied to field of display, light-emitter, display board for sign lamp, or light source for liquid crystal display.

Brief Description of the Figures

10

Figure 1. Absorption spectra of complexes **1b** & **2b** in CH_2Cl_2

Figure 2. Emission spectra of complex **1b** in CH_2Cl_2 and as thin film at 298 K

Figure 3. Emission spectra of complex **2b** in CH_2Cl_2 and as thin film at 298 K

Figure 4. TGA thermograms of complexes **1b** and **2b** under nitrogen and air

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Figure 5. Schematic diagram of OLED in present invention

Figure 6a. Electroluminescent spectrum of Device A containing complex **1b** (doping level 0.3 wt%)

Figure 6b. Current density-voltage-luminance curve of Device A containing complex **1b** (doping level 0.3 wt%)

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Figure 7a. Electroluminescent spectrum of Device B containing complex **1b** (doping level 1.0 wt%)

Figure 7b. Current density-voltage-luminance curve of Device B containing complex **1b** (doping level 1.0 wt%)

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Figure 8. Electroluminescent spectrum of Device C containing complex **1b** (doping level 2.0 wt%)

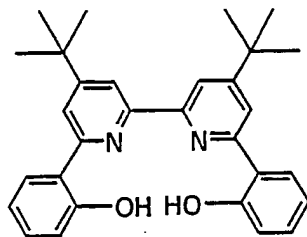
Detailed Description of the Invention

The inventions are generally related to syntheses, spectral characterization, phosphorescence, light-emitting properties of the new light-emitting materials, and their applications in OLEDs. The examples are set forth to aid in an understanding of the inventions but are not intended to, and should not be interpreted to, limit in any way the invention as set forth in the claims which follow thereafter.

The examples given illustrate the synthetic methods of ligands **1a** and **2a**, and the platinum complexes **1b** and **2b**. The quadridentate ONNO-type ligands **1a** and **2a** were prepared by modification of a literature procedure (*J. Chem. Soc., Perkin Trans. 2*, 863, (1998)). Another example of the preparation of ONNO-type ligands has been reported (US Patent 6,177,419).

EXAMPLE 1

Synthesis of **1a**



1a

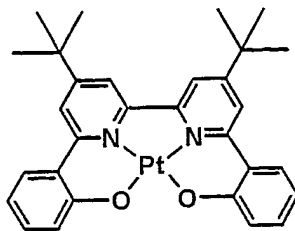
A mixture of 6,6'-bis(2-methoxyphenyl)-4,4'-bis(*tert*-butyl)-2,2'-bipyridine (1 g) in hydrobromic acid (47 %, 20 mL) was refluxed for 12 hours. This was cooled to room temperature and was neutralized with an aqueous saturated Na₂CO₃ solution at room temperature. The organic product was extracted with chloroform and the extracts were washed with deionized water (50 mL × 2), dried over anhydrous Na₂SO₄, and a solid residue was obtained by removal of solvent. Crystalline product of **1a** was obtained by recrystallization from a methanol/dichloromethane solution. EI-MS (*m/z*): 452 [*M*]⁺. ¹H NMR (CDCl₃, δ, ppm):

14.45 (2H, s, OH), 8.16 (2H, d, $J = 1.4$ Hz, ArH), 7.97 (2H, d, $J = 1.3$ Hz, ArH), 7.90 (2H, dd, $J = 8.0$ Hz, $J = 1.4$ Hz, ArH), 7.34 (2H, td, $J = 8.4$ Hz, $J = 1.5$ Hz, ArH), 7.07 (2H, dd, $J = 8.2$ Hz, $J = 1.6$ Hz, ArH), 6.96 (2H, td, $J = 8.1$ Hz, $J = 1.2$ Hz, ArH), 1.47 (18H, s, ^tBu). ¹³C NMR (CDCl₃, δ , ppm): 163.3, 159.7, 157.5, 152.2, 131.5, 126.5, 119.2, 118.9, 118.4, 116.4, 35.6, 30.6.

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EXAMPLE 2

Synthesis of 1b

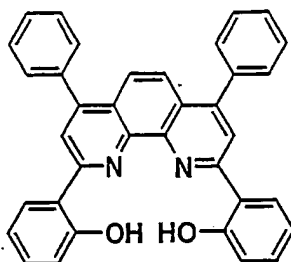


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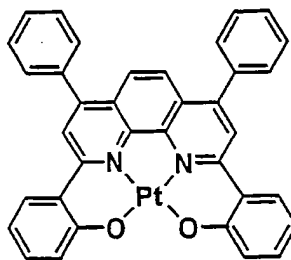
1b

The synthetic method of metal complex **1b** is described. A mixture of NaOMe (0.014 g, 0.25 mmol) and the ligand **1a** (0.113 g, 0.25 mmol) in methanol (20 mL) was stirred for 2 hours. An acetonitrile solution (20 mL) of Pt(CH₃CN)₂Cl₂ (0.25 mmol) was added to the methanolic suspension, which was refluxed for 24 hours. The resulting suspension was filtered and concentrated to about 5 mL. Upon addition of diethyl ether, a brown-yellow solid was obtained. The crude product was recrystallized by diffusion of diethyl ether into a dichloromethane solution to afford yellow crystals. FAB-MS (m/z): 645 [M]⁺, 1292 ($2M^+ + 2$), 1938 ($3M^+ + 3$). ¹H NMR (CDCl₃, δ , ppm): 8.32 (d, 2H, $J = 1.41$ Hz ArH), 8.01 (d, 2H, $J = 7.25$ Hz, ArH), 7.85 (d, 2H, $J = 1.68$ Hz, ArH), 7.48 (dd, 2H, $J = 7.38$ Hz, $J = 1.13$ Hz, ArH), 7.38 (td, 2H, $J = 5.35$, 1.61 Hz, ArH), 6.79 (td, 2H, $J = 5.40$, 1.35 Hz, ArH), 1.54 (s, 18H, ^tBu). ¹³C NMR (CDCl₃, δ , ppm): 162.745, 159.105, 155.291, 149.851, 131.269, 128.005, 124.060, 120.465, 120.402, 116.302, 116.148, 30.402, 29.715. FTIR (KBr, cm⁻¹): 3086 w, 2953 m, 1612 w, 1528 s, 1351 s, 1034 m, 885 w, 723 m.

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EXAMPLE 3**Synthesis of 2a****2a**

In a 100 mL round-bottom flask equipped with a reflux condenser, 2,9-bis(2-methoxyphenyl)-4,7-diphenyl-1,10-phenanthroline (finely ground, 2 g, 3.7 mmol) and pyridinium hydrochloride (4.23 g, 37 mmol) were mixed. The mixture was heated under nitrogen flow to 210 °C for 36 hours. After cooling, water (30 mL) was added and the aqueous solution was extracted with chloroform (3 × 30 mL). Combined organic extracts were washed with saturated sodium bicarbonate solution (5 × 30 mL) and water (3 × 30 mL), dried over anhydrous magnesium sulfate and evaporated to give a bright yellow solid. Chromatography over silica gel using n-hexane: dichloromethane (1:2) as eluent afforded 0.99 g of a yellow solid. FAB-MS (m/z): 517 [M+H]⁺. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 14.69 (2H, s, OH), 8.52 (2H, s, ArH), 8.41 (2H, dd, J = 8.0, 1.3 Hz, ArH), 7.90 (2H, s, ArH), 7.71 (4H, d, J = 7.4 Hz), 7.64 (6H, m, ArH), 7.43 (2H, td, J = 7.7, 1.5 Hz, ArH), 7.10 (2H, dd, J = 7.4 Hz, 1.3 Hz, ArH), 7.04 (2H, td, J = 7.5, 1.3 Hz, ArH). ¹³C NMR (600 MHz, CDCl₃): δ = 160.5, 157.7, 150.3, 142.8, 137.8, 132.2, 129.6, 128.9, 128.8, 127.1, 125.7, 123.7, 120.6, 119.4, 119.2, 118.9.

EXAMPLE 4**Synthesis of 2b****2b**

K_2PtCl_4 (0.08 g, 0.19 mmol) and **2a** (0.1 g, 0.19 mmol) were refluxed in glacial acetic acid (10 mL) for 2 days. After cooling, the resulting suspension was collected by filtration, washed with acetic acid and water successively and then dried under vacuum to afford a brown solid. The crude product was purified by chromatography on a silica gel column with dichloromethane as eluent. The product was recrystallized by slow evaporation of a dichloromethane solution to afford red crystals. FAB-MS: $m/z = 710 [M+H]^+$. 1H NMR (270 MHz, DMSO- d_6) 8.81 (2H, s, ArH), 8.56 (2H, d, $J = 8.9$ Hz, ArH), 8.01 (2H, s, ArH), 7.86 (4H, m, ArH), 7.71 (6H, dd, $J = 4.9, 2.0$ Hz, ArH), 7.44 (2H, t, $J = 7.4$ Hz, ArH), 7.24 (2H, d, $J = 8.2$ Hz, ArH), 6.80 (2H, t, $J = 7.6$ Hz, ArH).

The spectral characteristics of the platinum complexes **1b** and **2b** according to this invention are shown in Table 1. For complex **1b**, strong absorption bands at 250-350 nm ($\epsilon = 38400$ - 17500 $dm^3mol^{-1}cm^{-1}$) and a moderately intense absorption band at λ_{max} 398 nm ($\epsilon = 10800$ $dm^3mol^{-1}cm^{-1}$) are observed (Figure 1). In addition, a broad absorption band can be found at ca. 480 nm (2800 $dm^3mol^{-1}cm^{-1}$). For complex **2b** (Figure 1), several vibronic transitions at 291-375 nm ($\epsilon = 39200$ to 24700 $dm^3mol^{-1}cm^{-1}$) and a broad band at 504 nm ($\epsilon = 7200$ $dm^3mol^{-1}cm^{-1}$) are observed in CH_2Cl_2 .

Table 1. UV/vis absorption data of **1b** and **2b** in CH_2Cl_2

| Complexes | $\lambda_{max} / nm (\epsilon / 10^4 \times dm^3mol^{-1}cm^{-1})$ |
|-----------|--|
| 1b | 255 (3.80), 315 (1.75), 400 (0.82), 480 (0.25), 505 (0.22) |
| 2b | 291 (3.92), 315 (3.40), 325 (3.23), 352 (2.58), 375 (2.47), 420 (0.52), 488 (0.67), 504 (0.72) |

The photoluminescence (PL) of the platinum complexes **1b** and **2b** in solution and as thin film are summarized in Table 2. In Figure 2, the 298 K structureless emission of complex **1b** are observed at 595 and 599 nm in CH_2Cl_2 and as thin film respectively. The PL properties of complex **2b** in solution and as thin film are shown in Figure 3. The emission maximum of **2b** in thin film is shifted by 1704 cm^{-1} compared to that in solution. Meanwhile, complexes **1b** and **2b** exhibit lifetimes of 1.9 and 5.3 μs in CH_2Cl_2 and luminescent quantum yields of 0.1 and 0.6 (with $Ru(bpy)_3Cl_2$ as reference standard) respectively.

Table 2. PL properties of complexes **1b** and **2b** in solution and as thin film

| Complexes (Measuring medium / Temperature) | Emission (Maximum / nm) | Lifetime (μ s) | Quantum yield |
|---|-------------------------|---------------------|---------------|
| 1b (CH_2Cl_2 / 298 K) | 595 | 1.9 | 0.1 |
| 1b (Thin Film / 298 K) | 599 | / | / |
| 2b (CH_2Cl_2 / 298 K) | 586 | 5.3 | 0.6 |
| 2b (Thin Film / 298 K) | 651 | / | / |

concentration = $1 \times 10^{-5} \text{ mol dm}^{-3}$

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The TGA thermograms of complexes **1b** and **2b** are shown in Figure 4. Both the complexes demonstrate high thermal stabilities in nitrogen and air at heating rate of $15^\circ\text{C}/\text{min}$. Complex **2b** is stable up to 536°C in nitrogen and 379°C in air. The on-set temperatures of **1b** are at 438°C in nitrogen and 382°C in air. These observations reveal that these light-emitting materials can be sublimed and stable at vacuum deposition conditions in preparation of OLEDs.

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An electroluminescent device according to this invention is schematically illustrated in Figure 5. As examples of the present invention, OLEDs with configurations of ITO / NPB (α -naphthylphenylbiphenyl amine) (500 Å) / [0.3 wt% (device A), 1 wt% (device B), or 2 wt% (device C) of complex **1b**]:Bepp₂ (400 Å) / LiF (15 Å) / Al (2000 Å) were prepared. The fabrication of device A (0.3 wt% of **1b**) follows:

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EXAMPLE 5

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The device A was assembled as follows: indium tin oxide (ITO) electrode with sheet resistance of $20\Omega/\text{square}$ on glass substrate, a hole transport material NPB (α -naphthylphenylbiphenyl amine) with thickness of 500 Å, an emitting layer made of mixture of 0.3 wt.% complex **1b** and blue luminescent material Bepp₂ (beryllium bis(2-(2'-hydroxyphenyl)pyridine) with 400 Å thickness, an enhanced charge transport layer LiF with thickness of 15 Å, and aluminum layer with 2000 Å thickness. The metal and organic layers were laminated in sequence under 5×10^{-6} mbar without breaking vacuum between different vacuum deposition processes. The layers were deposited at rates of 2 or 5 Å per second. The

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emissive area of the device as defined by overlapping area of cathode and anode was 3×3 mm². The ITO coated glass slides were cleaned with organic solvents (acetone-isopropanol-methanol), deionized water, followed by ultra-violet-ozone cleaner. EL spectra and current density-voltage-luminance characteristics of the devices were measured with a spectrophotometer and a computer-controlled direct-current power supply respectively at room temperature.

For these examples, the device external efficiencies increase when the doping concentration levels of complex **1b** were adjusted from 2 to 0.3 wt%. The specific examples are further illustrated as follows:

EXAMPLE 6

The performances of device **A** with 0.3 wt% doping level of complex **1b** are shown in Figures 6a and 6b. Two intense EL emissions at 453 and 540 nm are observed when the device was driven under forward bias. The current density-voltage-luminance characteristics curves of device **A** are also shown. The turn-on voltage is approximately 6-7 V. The maximum efficiency of the device was 4.1 cd/A at luminance of 2849 cd/m². The maximum luminance of 9325 cd/m² was obtained at driving voltage of 10 V. The EL color of device **A** is yellow (CIE coordinates: $x = 0.33$, $y = 0.47$).

EXAMPLE 7

The performances of device **B** with 1.0 wt% doping level of complex **1b** are shown in Figures 7a and 7b. The device exhibits an intense EL emission peak at 546 nm and a weak emission at 457 nm. The onset voltage of device **B** was approximately at 6-7 V. The efficiency and maximum luminance were 1.9 cd/A at luminance of 1927 cd/m² and 6563 cd/m² at driving voltage of 9.5 V respectively. The EL color of device **B** is yellow (CIE coordinates: $x = 0.39$, $y = 0.54$).

EXAMPLE 8

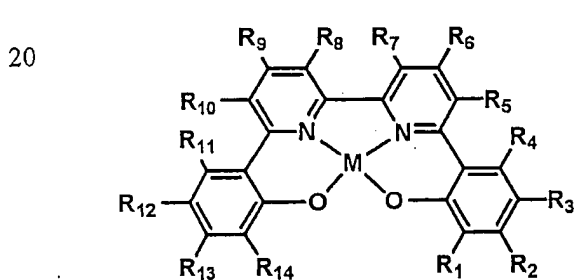
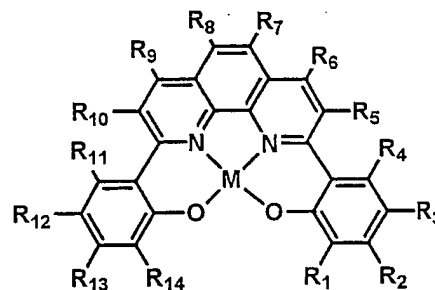
Device **C** with 2.0 wt% doping level of complex **1b** exhibits an intense EL emission peak at 548 nm with an extremely weak emission at around 450 nm (Figure 8); EL efficiency of 1.5 cd/A was detected. Luminance of 6450 cd/m² was observed at driving voltage of 12 V.

The EL color of device C is yellow (CIE coordinates: $x = 0.42$, $y = 0.56$).

Typically, doping level of greater than 5 % is reported to achieve dopant emission in organic or polymeric light-emitting devices. In this invention, the OLEDs show virtually complete
5 emission of complex 1b when the doping level is around 2% and the efficiencies of devices increase from 1.5 to 4.1 cd/A when the doping levels of complex are decreased from 2.0 to 0.3 wt%.

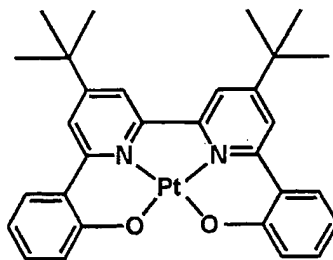
What is claimed:

1. In an organic light-emitting device containing a heterostructure for producing electroluminescence, an emissive layer, comprising at least a host material and an emissive molecule, present as a dopant in said host material, wherein the said emissive molecule is selected from metal complexes bearing a quadridentate ligand containing at least one pyridine or substituted pyridine group.
2. The emissive layer of claim 1, wherein said emissive molecule is selected from metal complexes bearing a quadridentate ONNO-type ligand, where NN is 2,2'-bipyridine or substituted 2,2'-bipyridine or 1,10-phenanthroline or substituted 1,10-phenanthroline.
3. The emissive layer of claim 1, wherein the metal of said metal complexes is selected from Group 10.
4. The emissive layer of claim 1, wherein said emissive molecule can have a chemical structure represented by Formula I and II:

**I****II**

wherein M represents a Group 10 metal (including platinum) and R₁-R₁₄ are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups.

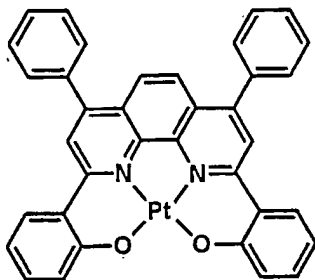
5. The emissive layer of claim 4, wherein said emissive molecule is presented as a dopant in said host material in low concentration, including 0.3 to 2.0 weight % based on weight of host material.
- 5 6. The emissive layer of claim 4 that produces electroluminescence of yellow color.
7. A method for turning color (CIE coordinates) emitted by an organic light-emitting device comprising emissive layer of claim 5.
- 10 8. The emissive layer of claim 4, wherein said the host material is beryllium bis(2-(2'-hydroxyphenyl)pyridine) (Bepp₂).
9. The emissive layer of claim 4, wherein the said host material and said emissive molecule can be deposited as a thin layer by method of sublimation or vacuum deposition or vapor deposition or spin-coating or other methods.
- 15
10. The emissive molecule is represented by Formula I in accordance with claim 4, wherein the R₁-R₅, R₇-R₈ and R₁₀-R₁₄ groups are proton atoms, R₆ and R₉ groups are *tert*-butyl groups, and M is platinum, namely:



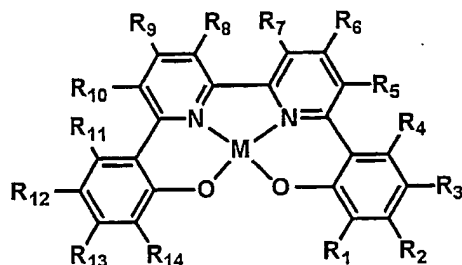
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11. The emissive molecule is represented by Formula II in accordance with claim 4, wherein the R₁-R₅, R₇-R₈ and R₁₀-R₁₄ groups are proton atoms, R₆ and R₉ groups are phenyl groups, and M is platinum, namely:

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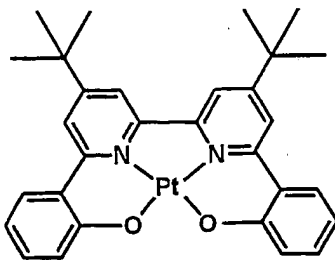
12. A method for the preparation of a light-emitting material having a structure represented by Formula I:



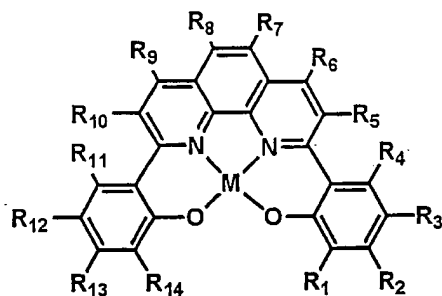
I

- wherein M represents a Group 10 metal (including platinum) and R_1 - R_{14} are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups.

13. The method in accordance with claim 12 wherein the R_1 - R_5 , R_7 - R_8 and R_{10} - R_{14} groups are proton atoms, R_6 and R_9 groups are *tert*-butyl groups, and M is platinum, namely:



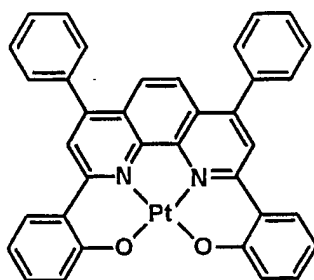
14. A method for the preparation of a light-emitting material having a structure represented by Formula II:

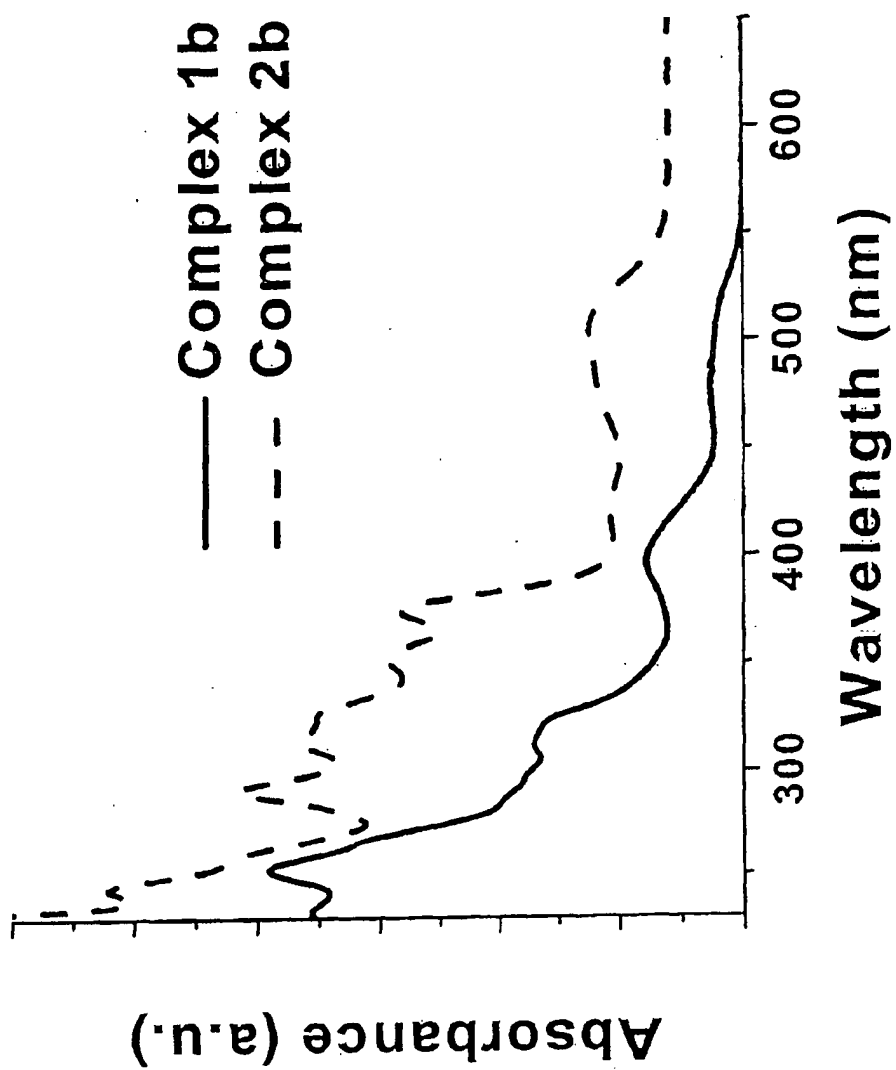


II

wherein M represents a Group 10 metal (including platinum) and R₁-R₁₄ are each independently selected from the group consisting of hydrogen; halogen; alkyl; substituted alkyl; aryl; substituted aryl, with substituents selected from the group consisting of halogen, lower alkyl and recognized donor and acceptor groups.

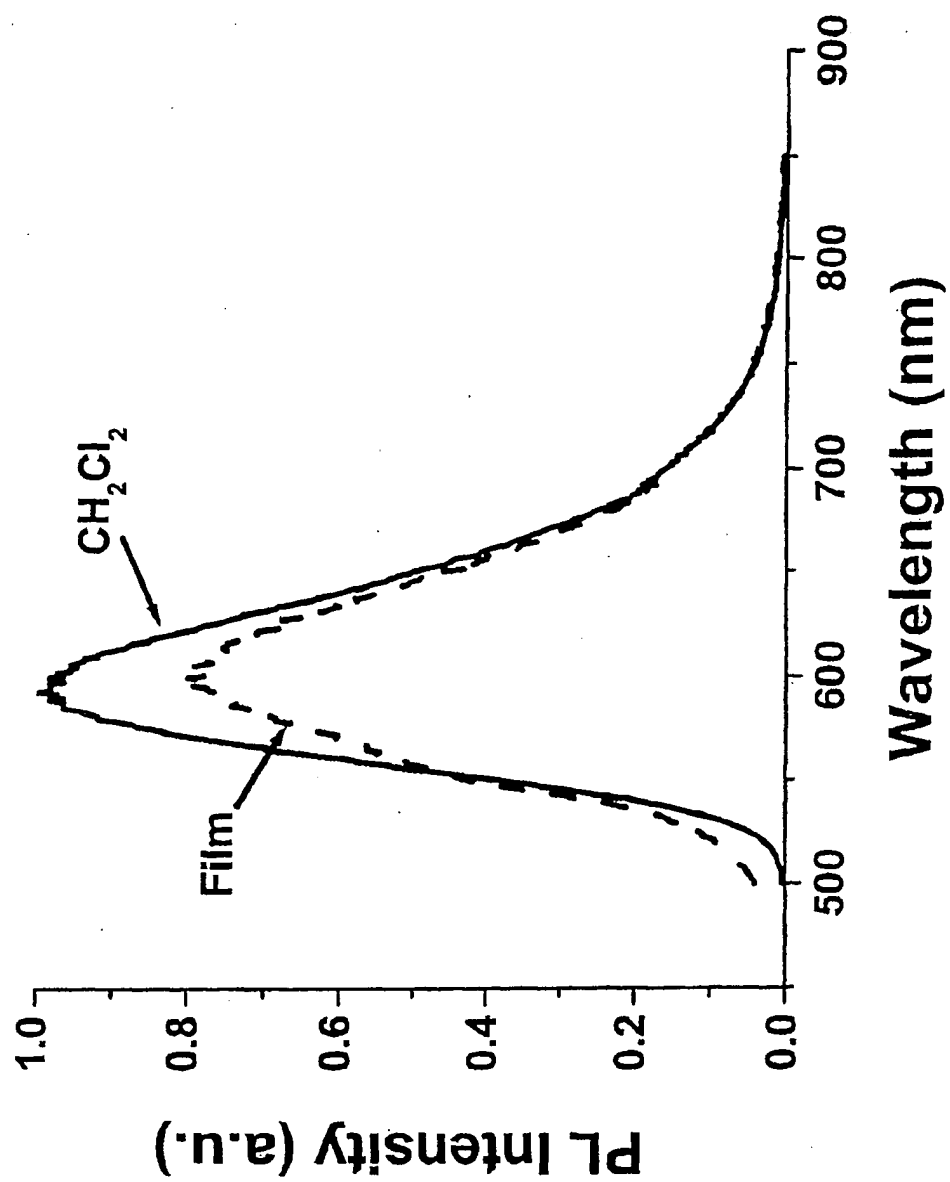
15. The method in accordance with claim 14 wherein the R₁-R₅, R₇-R₈ and R₁₀-R₁₄ groups are proton atoms, R₆ and R₉ groups are phenyl groups, and M is platinum, namely:





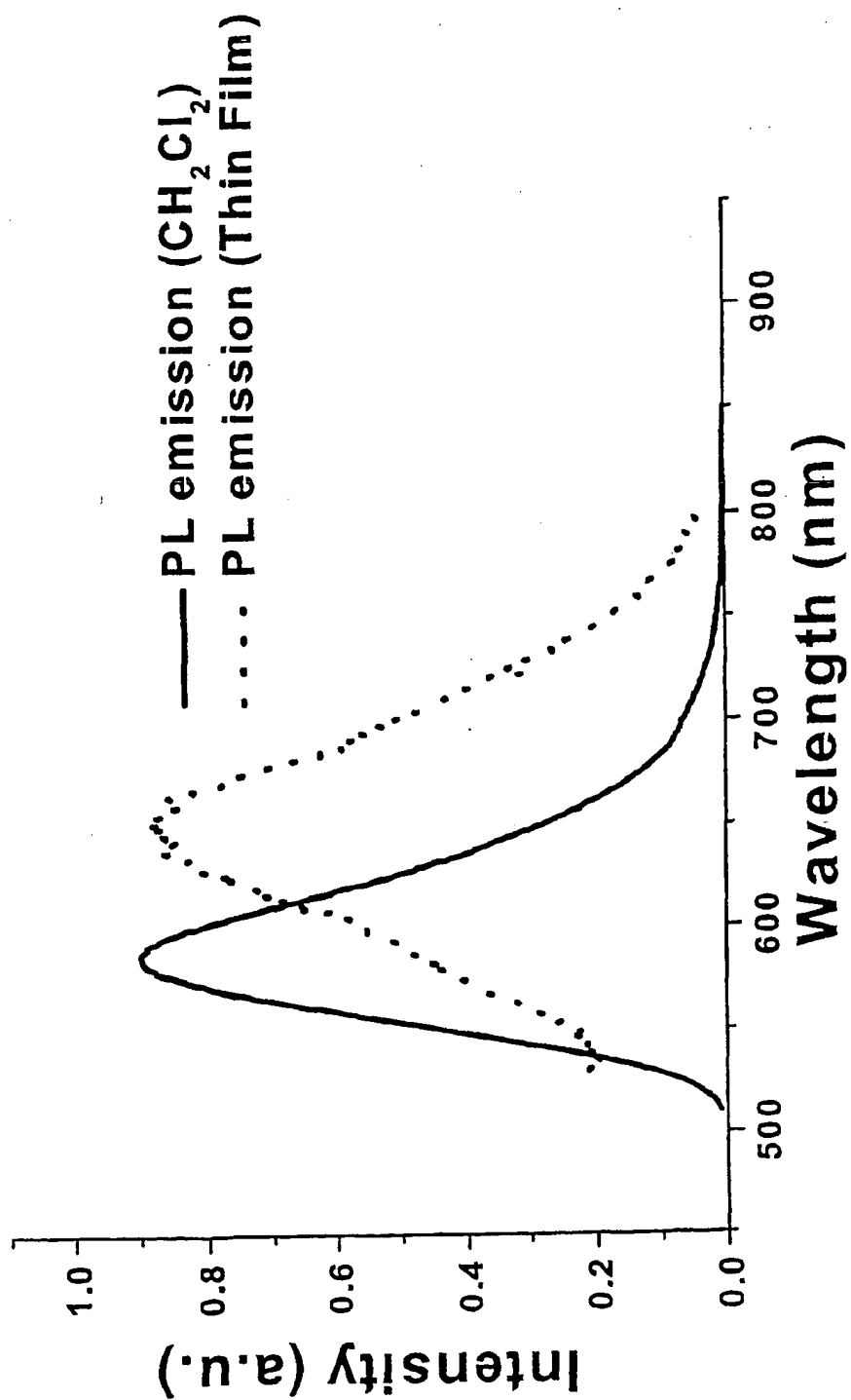
Absorption spectra of complexes 1b & 2b in CH_2Cl_2

FIG. 1



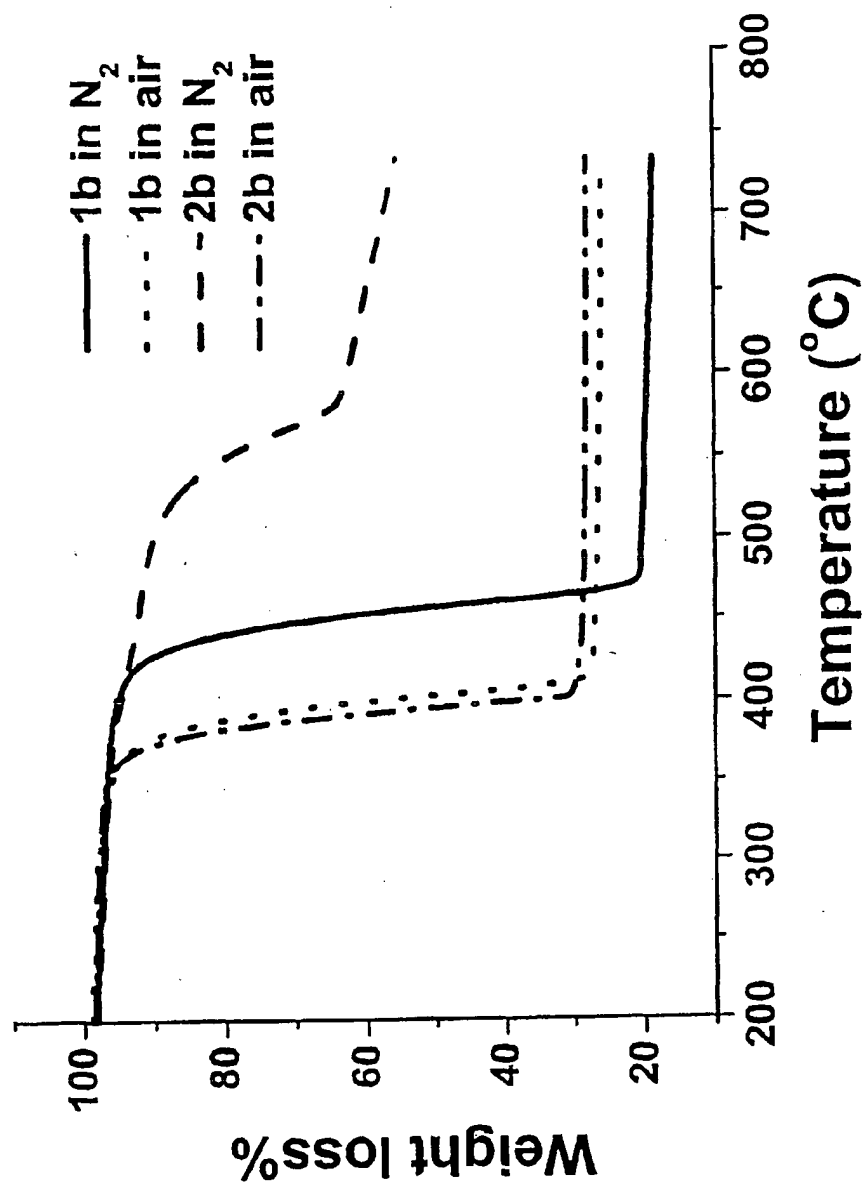
Emission spectra of complex 1b in CH₂Cl₂ and as thin film at 298 K

FIG. 2



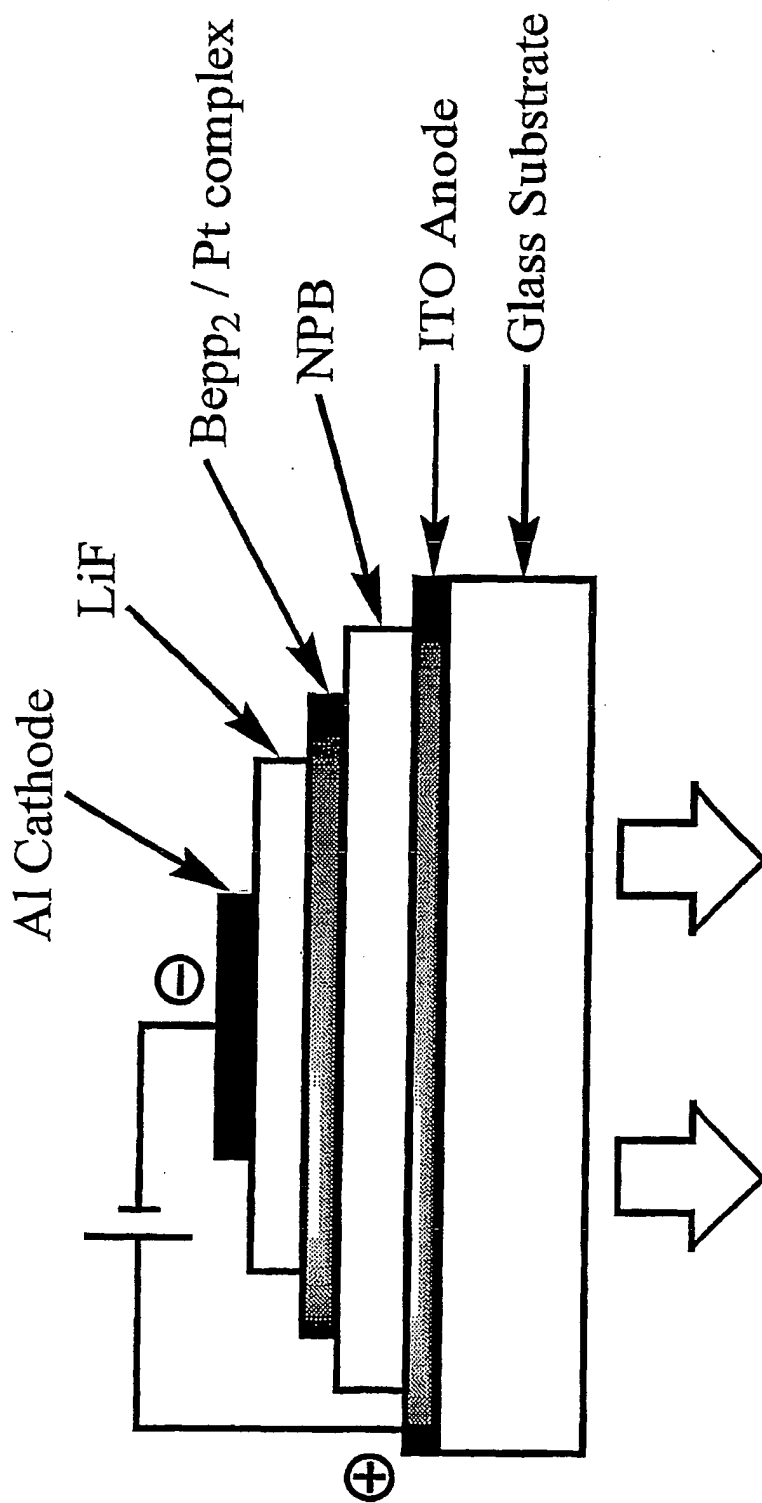
Emission spectra of complex 2b in CH₂Cl₂ and as thin film at 298 K

FIG. 3



TGA thermograms of complexes 1b and 2b under nitrogen and air

FIG. 4



Schematic diagram of OLED in present invention

FIG. 5

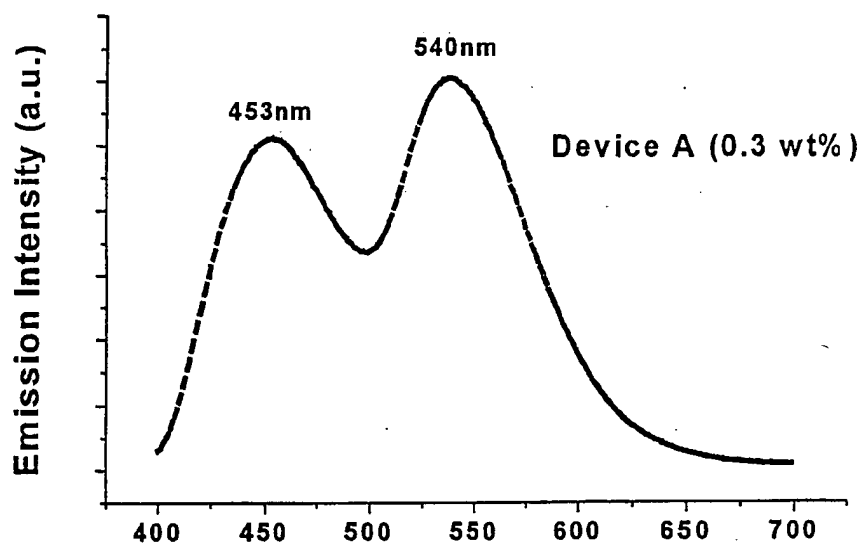


Figure 6a. Electroluminescent spectrum of Device A containing complex 1b (doping level 0.3 wt%)

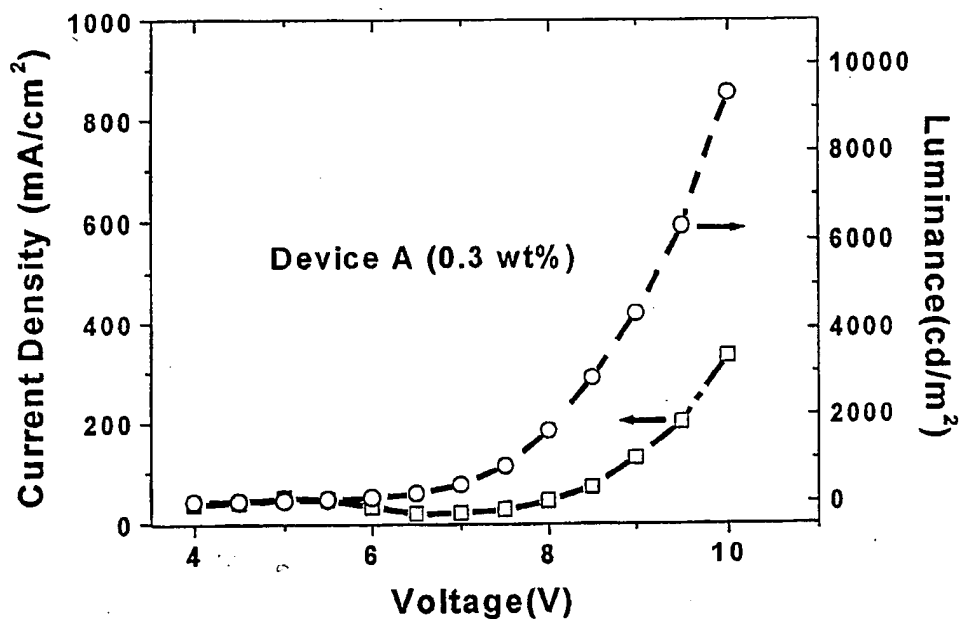


Figure 6b. Current density-voltage-luminance curve of Device A containing complex 1b (doping level 0.3 wt%)

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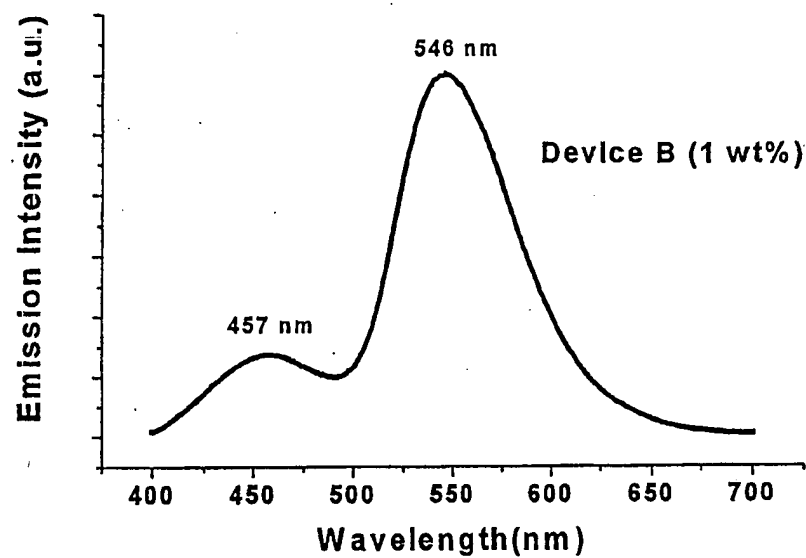


Figure 7a. Electroluminescent spectrum of Device B containing complex 1b (doping level 1.0 wt%)

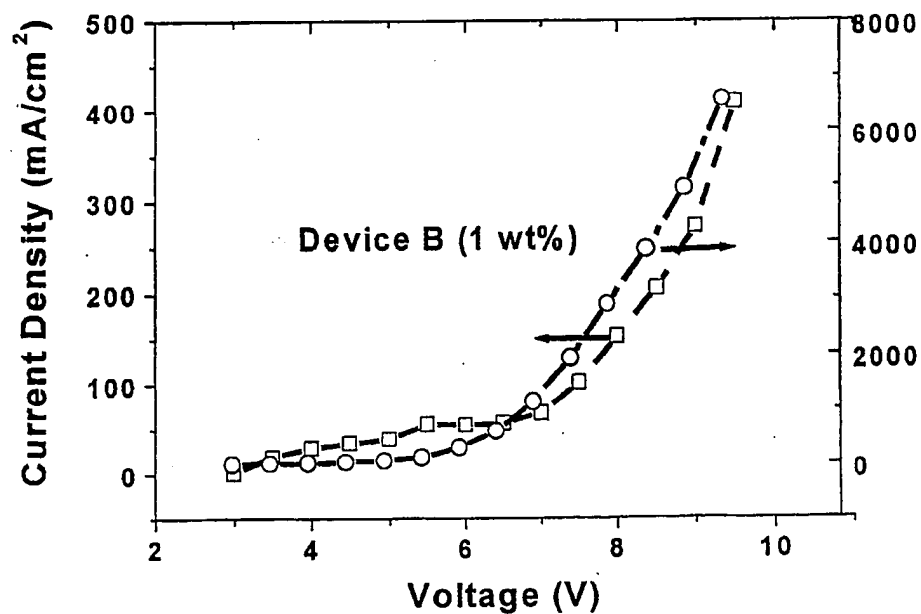
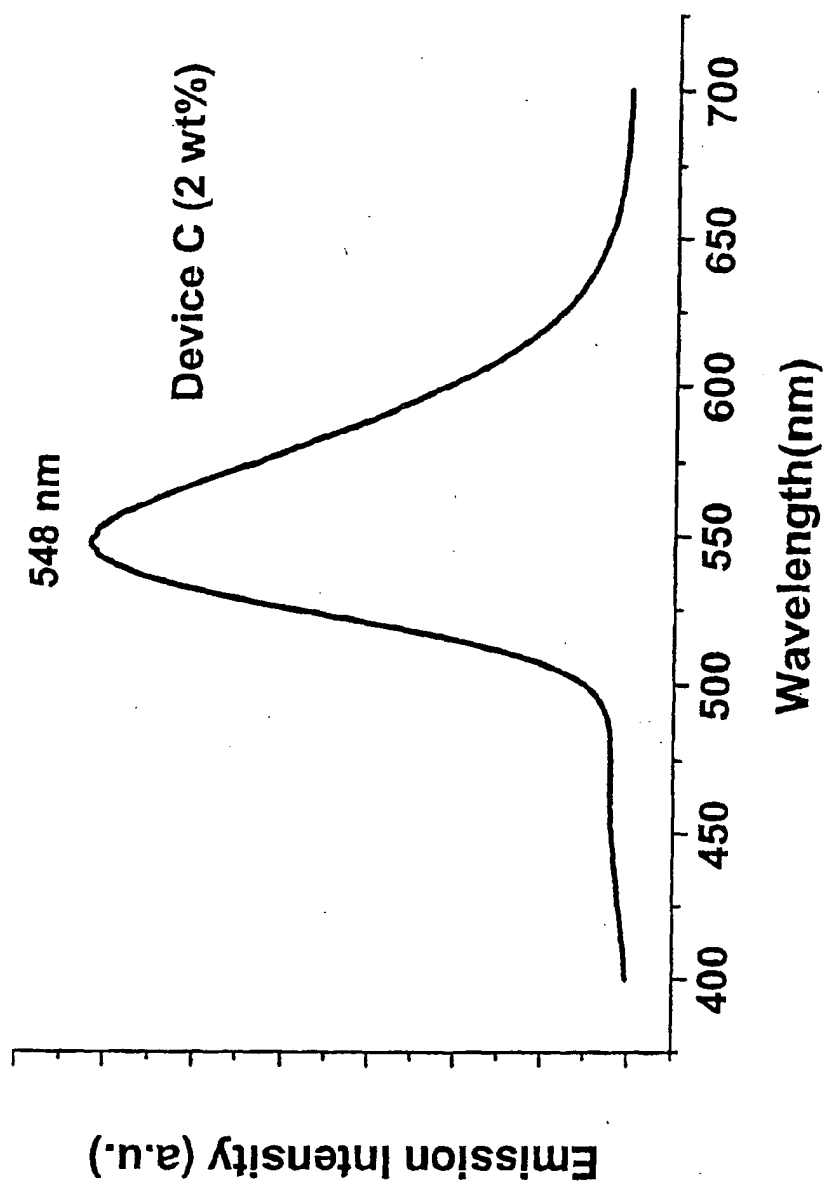


Figure 7b. Current density-voltage-luminance curve of Device B containing complex 1b (doping level 1.0 wt%)

FIG. 7



Electroluminescent spectrum of Device C containing complex 1b (doping level 2.0 wt%)

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN03/00221

A. CLASSIFICATION OF SUBJECT MATTER

C07F15/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

WPI: tetradentate*pyridine CNPAT: 联吡啶*四齿 Chemical Abstract: tetradentate*pyridine

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CNPAT, CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | Chemical Abstracts: 135:152935. published in the year of 2001. | 1 |
| A | Tsukada, N. et al, Synthesis and crystal structure of tristed dinuclear η^3 -allylpalladium complexes containg tetradentate nitrogen ligands | 2-15 |
| X | Chemical Abstracts: 134:50644. published in the year of 2000. | 1 |
| A | Predetermined chirality at metal centers of various coordination geometries: a chiral cleft ligand for tetrahedral (T-4), square-planar(SP-4), trigonal-bipyramidal(TB-5), square-pyramidal(SPY-5), and octahedral(OC-6) complexes. Mamula, Olimpia et al. | 2-15 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | |
|--|--|
| * Special categories of cited documents: | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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| "O" document referring to an oral disclosure, use, exhibition or other means | |
| "P" document published prior to the international filing date but later than the priority date claimed | "&" document member of the same patent family |

Date of the actual completion of the international search
17.July 2003(17.07.2003)

Date of mailing of the international search report

24 JUL 2003 (24.07.03)

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